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A new method for the determination of molecular and intramolecular relaxation times.

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A new method for analysing the data on dielectric constant (ϵ') and dielectric loss factor (ϵ'') measured at different microwave frequencies in the case of dilute solutions of anisole and *o*-nitrophenol in non polar solvents and anisole in the liquid state in terms of two Debye terms for determining the relaxation times of the whole molecule (τ_1) and of the rotable polar group (τ_2) and their relative contribution factors C_1 and C_2 has been described. It is pointed out that the present analytical method is more straightforward compared to the generally adopted trial and error method of analysis.

1. Introduction

The dielectric constant (ϵ') and dielectric loss (ϵ'') of anisole in different microwave frequency regions and at different temperatures have been investigated by many workers in solutions in non-polar solvents (Hase 1953, Klages & Zenteck 1961, Grubb & Smyth 1961, Forrest & Smyth, 1964, Farmer, Holt & Walker 1966, Kastha, Dutta & Roy 1967) and in the pure liquid state (Roberti & Smyth 1960, Vaughan, Bergmann & Smyth 1961 ; Vaughan & Smyth 1961). Similar investigations in the case of ortho nitrophenol and a number of other phenolic compounds in dilute solutions in non-polar solvents have recently been reported by Magee & Walker (1966). The results have been interpreted in terms of two Debye relaxation mechanisms with the help of the following equations,

$$\frac{\epsilon'-\epsilon_\infty}{\epsilon_0-\epsilon_\infty}=\frac{C_1}{1+\omega^2\tau_1^2}+\frac{C_2}{1+\omega^2\tau_2^2} \qquad \ldots 1\ (a)$$

and

$$\frac{\epsilon''}{\epsilon_0-\epsilon_\infty}=\frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2} \qquad \ldots 1\ (b)$$

with $C_1+C_2=1$; where τ_1 is the time of relaxation for the orientation of the whole molecule and τ_2 is the time of relaxation of the rotating polar group, C_1 and C_2 are the relative contributions to overall dielectric constant and loss-values due respectively to the two relaxation mechanisms and all other symbols have their usual significance.

The analysis of the results have usually been made by assuming reasonable values of τ_1, τ_2 and C_2 (sometimes the value of ϵ_∞ is also slightly varied) and then comparing the values of ϵ' and ϵ'' calculated with the help of equation (1) with those of the respective experimental values at different microwave frequencies. Though there is fair agreement in the results obtained in any particular investigation, the values of τ_2 and C_2 obtained by different workers vary considerably. For example, in the case of dilute solutions of anisole in benzene the value of τ_2 reported by various workers varies between $6.5.\times10^{-12}$ sec (Forrest & Smyth, 1964) to 0.8×10^{-12} sec (Klages & Zenteck 1961) and the corresponding values of C_2 are 0.8 and 0.2 respectively.

In the case of pure liquid the data are fewer. Vaughan & Smyth (1961) have analysed the dielectric constant and loss data at the microwave frequencies measured by Roberti & Smyth (1960) in the pure liquid state at 20°C with help of equations (1) and have obtained the value of τ_2 as 3.7×10^{-12} sec and C_2 as 0.2.

Recently, Kastha (1968) has pointed out that though the equation (1) are approximately valid in the case of very dilute solutions of polar molecules e. g. anisole, in non-polar solvents, in the case of the pure liquids, these equations are not applicable and hence the values of τ_1, τ_2 and C_2 obtained with their help will not be the true ones. In the present paper the results reported in the existing literature have been examined critically and a method by which the trial and error method of determining the τ_1, τ_2 and C_2 values is avoided has been outlined.

2. Theory of the method

Kastha (1968) has given the following functional relations between ϵ', ϵ'', τ_1 and τ_2 in the case of polar liquids consisting of molecules, like anisole, or solutions of such polar compounds in non polar solvents :

$$\frac{(\epsilon_0+2)[(\epsilon'-\epsilon_\infty)(\epsilon'+2)+\epsilon''^2]}{(\epsilon_0-\epsilon_\infty)[(\epsilon'+2)^2+\epsilon''^2]}=\frac{C_1}{1+\omega^2\tau_1^2}+\frac{C_2}{1+\omega^2\tau_2^2} \qquad \ldots 2\text{ (a)}$$

and

$$\frac{(\epsilon_\infty+2)(\epsilon_0+2)\epsilon''}{(\epsilon_0-\epsilon_\infty)[(\epsilon'+2)^2+\epsilon''^2]}=\frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2} \qquad \ldots 2\text{ (b)}$$

with $C_1+C_2=1$.

In the case of very dilute solutions in non polar solvents for which $\epsilon'\approx\epsilon_0\simeq\epsilon_\infty$ and ϵ'' is very small these equations reduce to those given in equations 1 (a) and 1 (b). Denoting the expressions on the left hand side of equation 1 (a) or 2 (a) by a and those of equations 1(b) or 2 (b) by b and

putting $\omega\tau_1=X_1$ and $\omega\tau_2=X_2$ we get,

$$a = \frac{C_1}{1+X_1^2} + \frac{C_2}{1+X_2^2}$$

and $$b = \frac{C_1X_1}{1+X_1^2} + \frac{C_2X_2}{1+X_2^2}$$

From these relations we obtain

$$C_1=\frac{(b-aX_2)(1+X_1^2)}{X_1-X_2};\quad C_2=\frac{(a-bX_1)(1+X_2^2)}{X_1-X_2} \qquad \ldots 3\ (a)$$

and $$a(1-a)-b^2=\frac{C_1C_2(X_1-X_2)^2}{(1+X_1^2)(1+X_2^2)} \qquad \ldots 3\ (b)$$

Equation 3 (b) takes care of the fact that for the existence of two relaxation times the condition $a(1-a)-b^2>0$ must be satisfied. Using the relation $C_1+C_2=1$, the following equation is obtained from 3 (a),

$\frac{1-a}{b} = X_1+X_2-\frac{a}{b}X_1X_2$; when dividing by ω we get

$$\frac{1-a}{b\omega} = \tau_1+\tau_2-\frac{a\omega}{b}\tau_1\tau_2 \qquad \ldots (4)$$

So if the values of $\frac{1-a}{b\omega}$ and $\frac{a\omega}{b}$ obtained from the experimental values of ϵ', ϵ'', ϵ_0 and ϵ_∞ at a certain temperature for different microwave frequencies are plotted as ordinate and abscissa respectively, a straight line graph will result from whose intercept and inclination the values of $\tau_1+\tau_2$ and $\tau_1\tau_2$ respectively are obtained. From these values the values of τ_1 and τ_2 are determined. The values of C_1 or C_2 are then obtained from the corresponding expressions on equation 3(a). If the C_1 or C_2 values obtained for the different microwaves frequencies are the same then the values of τ_1, τ_2, C_1 or C_2 are uniquely determined.

The method outlined above has been applied to a number of cases and short descriptions of the procedure adapted for the analysis of the experimental data and the results of the analysis are given in the following paragraphs.

3. Results

(a) Solution of anisole in cyclohexane : Farmer *et al* (1966) have measured the values of ϵ' and ϵ'' of solution of anisole in cyclohexane of

two different strengths at five microwave frequencies at 25°C and also the ϵ_0 and ϵ_∞ values of the solutions at the same temperature The a and b values calculated with the help of these data from the L H S expressions of equation (1) are given in table 1 (a) It is seen that the a or b value for the two solutions at any microwave frequency are different though according to the R H S expression of equation (1) they should be the same for both the solutions Accordingly, the mean values of a and b have been used to obtain the values of $\frac{1-a}{b\,\omega}$ and $\frac{a\,\omega}{b}$ which are entered in table 1(b)

Instead of a graphical evaluation of equation (4) the method of least squares for the best fit of the experimental data with the linear relation of equation (4) has been used to obtain the values of $\tau_1+\tau_2$ and $\tau_1\tau_2$ and hence of τ_1 and τ_2 The C_2 values obtained for different microwave frequencies are also shown in table 1(b) The values of τ_1, τ_2 and the most probable C_2 value obtained in this way are shown in table 1(c) along with those reported by Farmer, Holt and walker, (1966) for comparison

TABLE 1 (*a*)

ANISOLE IN SOLUTION IN CYCLOHEXANE TEMP 25°C
VALUE OF a AND b CALCULATED BY DIFFERENT METHODS

λ cm		L H S expressions of equation (1) using ϵ ϵ'' ϵ_0 and ϵ_∞ values of		R H S expression of equation (1) using	
		Farmer *et al* (1966) 05976 wt fraction	Farmer *et al* (1966) 0792 wt fraction	τ_1 τ_2 C_1 and C_2 values of this work	τ_1 τ_2 C_1 and C_2 values of Farmer *et al* (1966)
0 428	*a*	143	111	117	112
	b	286	289	288	291
0 860	*a*	286	333	315	314
	b	372	400	400	422
1 249	*a*	428	444	453	462
	b	414	444	429	447
1 850	*a*	428	555	599	616
	b	414	422	420	431
3 220	*a*	857	888	778	797
	b	376	344	356	354

TABLE 1 (*b*)

ANISOLE IN SOLUTION IN CYCLOHEXANE TEMP. 25°C

$\frac{1-a}{b\omega}$ AND $\frac{a\ \omega}{b}$ VALUES OBTAINED FROM MEAN a AND b VALUES OF COLUMNS (2) AND (3) OF TABLE 1 (*a*)

λ cm.	0 428	0.860	1.249	1.850	3.220
$1-a/b\omega \times 10^{12}$	6.91	8.17	8.71	11 93	6.63
$a\omega/b \times 10^{-12}$	.1949	1755	.1516	.1199	.1546
C_2	0.66	0.59	0.61	0.40	0.90

TABLE 1 (*c*)

ANISOLE IN SOLUTION IN CYCLOHEXANE TEMP. 25°C

Method	$\tau_1 \times 10^{12}$ sec.	$\tau_2 \times 10^{12}$ sec.	C_2
Present analytical method	15.4	4.77	0.59
Trial and error method Farmer *et al* (1966)	14.6	5.20	0.65

In order to find out how far the values of τ_1, τ_2, and C_2 obtained by the present methord reproduce the experimentally observed ϵ' and ϵ'' at different microwave frequencies, the values of a and b have been calculated with the R. H. S. expressions of equation (1) using these values and they have been compared with the a and b values obtained from the L. H. S. expressions of equation (1) using the experimental values of ϵ', ϵ'', ϵ_0 and ϵ_∞. These are shown in table 1 (a). In the same table are also included for comparison the values of a and b calculated from the R. H. S. expressions of equation (1) using the τ_1, τ_2, C_1, C_2 values reported by Farmer, Holt and Walker (1966). The agreement seems to be slightly better in the case of a and b values calculated with the data of the present work.

(b) Ortho nitrophenol in solution in paraxylene :

The ϵ' and ϵ'' values at four microwave frequencies in the case of .02056 M solution of *o*-nitophenol in *p*-xylene at 25°C along with the value of ϵ_0 and ϵ_∞ have been reported by Magee and Walker (1966). The a and b values calculated from the L. H. S. expressions of equation (1) using the experimental values of ϵ', ϵ'', ϵ_0 and ϵ_∞ are given in Table 2(a) and values of $\frac{1-a}{b\ \omega}$ and $\frac{a\ \omega}{b}$ are entered in table 2(b). The τ_1, τ_2 and the most probable C_2 values determined in the same way as described in the

case of solution of anisole in cyclohexane are presented in Tables 2(c) and 2(b) and in the former table the values of τ_1, τ_2 and C_2 obtained by Magee and Walker are shown for comparison.

TABLE 2 (*a*)

o-NITROPHENOL IN SOLUTION IN *p*-XYLENE TEMP. 25°C

VALUES OF a AND b CALCULATED BY DIFFERENT METHODS

λ cm.		L.H.S. expressions of equation (1) using ϵ', ϵ'', ϵ_0 and ϵ_∞ values of Magee & Walker (1966) .02056 M	R.H.S. expressions of equation (1) using τ_1, τ_2, C_1 and C_2 values of this work	τ_1, τ_2, C_1 and C_2 values of Magee & Walker (1966)
0.86	*a*	.1487	.1555	.1750
	b	.3120	.3134	.3137
1.25	*a*	.2477	.2503	.2665
	b	.3814	.3809	.3789
1.85	*a*	.3467	.3840	.3988
	b	.4309	.4382	.4353
3.22	*a*	.6439	.6170	.6315
	b	.4556	.4514	.4457

TABLE 2 (*b*)

o-NITROPHENOL IN SOLUTION IN *p*-XYLENE TEMP. 25°C

$\frac{1-a}{b\omega}$ AND $\frac{a\omega}{b}$ VALUES OBTAINED FROM a AND b VALUES OF COLUMN (2) OF TABLE 2 (*a*)

λ cm.	0.86	1.25	1.85	3.22
$1-a/b\omega \times 10^{12}$	12.46	13.09	15.24	13.37
$a\omega/b \times 10^{-12}$	.1043	.0979	.0859	.0827
C_2	0.18	0.20	0.17	0.24

TABLE 2 (*c*)

o-NITROPHENOL IN SOLUTION IN *p*-XYLENE TEMP. 25°C

Method	$\tau_1 \times 10^{12}$ sec.	$\tau_2 \times 10^{12}$ sec.	C_2
Present analytical method	15.8	4.87	0.20
Trial and error method (Magee & Walker 1966)	15.0	3.60	0.17

A comparison of the a and b values calculated from the R.H.S. of equation (1) with the a and b values determined from experimental data, which are all given in table 2(a), shows the true values of τ_1, τ_2 and C_2 are possibly closer to those obtained in the present investigation than those reported by Magee & Walker (1966).

(c) Anisole in the pure liquid state :

The ϵ' and ϵ'' values of liquid anisole at three microwave frequencies at 20°C and two other temperatures and the ϵ_0 and ϵ_∞ values have been measured by Roberti & Smyth 1960. These results have been analysed with the help of equation (1) by Vaughan & Smyth (1961) using $\epsilon_\infty=2.38$ (in place of the value of $n_D^2=\epsilon_\infty=2.30$). They reporterd that the values $\tau_1=13.3\times10^{-12}$ sec, $\tau_2=3.7\times10^{-12}$ sec and $C_2=0.20$ satisfactorily reproduces from the R.H.S. expressions of equations (1) the experimental values of ϵ' and ϵ'' measured at three microwave frequencies.

Kastha (1968) pointed out that equations (1) are not applicable to the case of polar liquids like anisole and therefore, the experimental results have been analysed by the present method (outlined in the case of solution of anisole in cyclohexane) using a and b values calculated from the experimental ϵ', ϵ'' and c_0 values and $\epsilon_\infty = 2.30$ with the help of the L.H.S. expressions of equations (2). The relevant data are given in tables 3 (a) and 3 (b).

TABLE 3 (*a*)

ANISOLE—PURE LIQUID TEMP. 20°C

VALUES a and b CALCULATED BY DIFFERENT METHODS

λ.cm.		L.H.S. expression of eqn. (2) using ϵ', ϵ'', ϵ_0 and $\epsilon_\infty=2.3$ values of Roberti & Smyth (1960)	R.H.S. expression of eqn. (2) using τ_1, τ_2, C_1 and C_2 values of this work
1.25	*a*	.5024	.5519
	b	.3612	.3551
3.22	*a*	.8153	.8128
	b	.3107	.3056
10.00	*a*	.9712	.9717
	b	.1336	.1362

TABLE 3 (*b*)

ANISOLE—PURE LIQUID TEMP. 20°C

$\frac{1-a}{b\omega}$ AND $\frac{a\omega}{b}$ VALUES OBTAINED FROM a AND b VALUES OF COLUMN (2) OF TABLE 3 (a)

λ cm	1 25	3 22	10 00
$1-a/b\omega$ x10^{12}	9 137	10 160	11 440
$a\omega/b$ x10^{-12}	2097	1536	1371
C_2	0 42	0 52	0 53

TABLE 3 (c)

ANISOLE—PURE LIQUID TEMP. 20°C

Method	τ_1 x10^{12} sec	τ_2 x10^{12} sec	C_2
Present analytical method	12 65	2 18	0 49
Trial and error method	13 30	3 75	0 20
Vaughan & Smyth (1961)			

The values of τ_1, τ_2 and the mean C_2 -value obtained from these calculations together with those given by Vaughan & Smyth (1961) are tabulated in table 3(c).

From table 3(a) it is seen that the agreement between the a and b values calculated from the experimental data (column 1) with those obtained from the R.H.S. expressions of equations (2) using the τ_1, τ_2, C_1 and C_2 values obtained in the present investigation are satisfactory. It is also noted from table 3 (c) that though the present values of τ_1 and τ_2 are somewhat smaller than those given by Vaughan & Smyth, the value of C_2 obtained in this investigation is much higher than that obtained by the latter authors. This difference in the evaluation of the relative contribution made by the relaxation mechanism of the methoxy group to overall dielectric constant and dielectric loss factor in the case of liquid anisole is due to the exact two terms Debye dispersion relations derived by Kastha (1968).

5. Conclusion

From the considerations presented above it may fairly be concluded that the present method of analysis yields values of τ_1, τ_2 and C_2 which closely satisfy the two term Debye dispersion relation used to describe the functional dependence of the dielectric constant and dielectric loss factor values at different microwave frequencies in the case of polar molecules with one rotatable polar group in different states of aggregation. Moreover, the method is straightforward and does not involve any guess work associated with the hitherto adopted trial and error method of analysis.

Finally, it need be pointed out that the calculated value of C_2 at some microwave frequencies in some cases indicates large relative errors in the values of a and b corresponding to the ϵ' and ϵ'' values measured at these microwave frequencies for the particular case in consideration.

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